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(71) Applicant: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.**
Carel van Bylandtlaan 30
NL-2596 HR Den Haag(NL)

(72) Inventor: **Drent, Eit**
Badhuisweg 3
NL-1031 CM Amsterdam(NL)

(74) Representative: **Aalbers, Onno et al**
P.O. Box 302
NL-2501 CH The Hague(NL)

(54) Process for the preparation of aldehydes.

(57) Process for the preparation of aldehydes by hydroformylation of an ethylenically unsaturated compound in the presence of (a) Pd, a Pd compound, Pt and/or a Pt compound, (b) an anion of a carboxylic acid with a $pK_a < 2$, and (c) a bidentate ligand R^1R^2-M-R-R^3R^4, wherein M is P, As or Sb, R a divalent organic bridging group having at least 3 C atoms in the bridge, and R^1, R^2, R^3 and R^4 are hydrocarbon groups.

PROCESS FOR THE PREPARATION OF ALDEHYDES

The invention relates to a process for the preparation of aldehydes by hydroformylation of an ethylenically unsaturated compound having at least five carbon atoms per molecule.

The hydroformylation of ethylenically unsaturated compounds, i.e. the catalytic addition of carbon monoxide and hydrogen to such compounds to produce aldehydes and/or alcohols is of great industrial importance. Aldehydes, in particular linear aldehydes, are very useful intermediates in industrial practice because of their terminal carbonyl group. For instance, they can be readily reduced to the corresponding primary alcohols and oxidized to the corresponding carboxylic acids. They also undergo addition and/or condensation reactions with a variety of chemicals such as hydrogen cyanide, alcohols, nitroparaffins as well as condensation reactions with themselves and other carbonyl-containing compounds. They can also be reacted with ammonia and derivatives thereof such as primary amines.

Much effort has been devoted over the years to the development of better catalytic systems, especially with a view to increase the linear/branched product ratio since this will have a positive influence on biodegradability problems encountered in various applications wherein aldehydes and/or alcohols are used as intermediates or starting materials, e.g. in surface-active compounds.

Since the classical cobalt carbonyl catalyst system which produces a large amount of branched chain products more advanced systems have been suggested comprising organophosphorus compounds, in particular tertiary phosphines or phosphites as ligands.

Not only ligands have been suggested as promoters and/or stabilizers for the original hydroformylation catalysts but also certain metal halides. For instance, it is known that Group IV A metal halides, in particular tin(II)-halides, preferably also containing a quaternary ammonium halide, can also be applied to improve the linear/branched ratio, especially when platinum is used as the main catalyst.

However, the use of Group IV A halides has the intrinsic drawback that normally a rather large excess of such compound is required which makes the working-up procedure of the process very unattractive. Moreover, it appears that high linear/branched product ratios can only be obtained at the expense of an increasing amount of alkanes being co-produced. It is therefore very desirable to develop a hydroformylation catalyst, which matches the speed of the cobalt-carbonyl based catalyst, whilst maintaining a high linear/branched product ratio at a minimal co-production of undesired alkanes.

It has now been found that ethylenically unsaturated compounds can selectively be hydroformylated to aldehydes with a very low amount of akanes being co-produced even at high linearity when the process is carried out in the presence of a specific ligand stabilized catalytic system.

Accordingly, the present invention provides a process for the preparation of aldehydes by hydroformylation of an alkenically unsaturated compound having at least 5 carbon atoms per molecule, in which an alkenically unsaturated compound is contacted with carbon monoxide and hydrogen in the presence of an aprotic solvent and a catalytic system based on

a) palladium, a palladium compound, platinum and/or a platinum compound,

b) an anion of a carboxylic acid with a $pK_a < 2$, measured in aqueous solution at 18 °C, and

c) a bidentate ligand of the general formula $R^1R^2\text{-M-R-M-}R^3R^4$, wherein M represents phosphorus, arsenic or antimony, R represents a divalent organic bridging group having at least three carbon atoms in the bridge, none of these carbon atoms carrying substituents that may cause steric hindrance, and R^1, R^2, R^3 and R^4 are similar or dissimilar optionally substituted hydrocarbon groups.

Suitable carboxylic acids are trichloroacetic acid, trifluoroacetic acid, dichloroacetic acid and difluoroacetic acid, trifluoroacetic acid being preferred.

Preferably the anion of the acid with a $pK_a < 2$ is present in the reaction mixture in a quantity of 0.01-150, in particular 0.1-100 and most preferably 1-50, moles per gram atom palladium and/or platinum. The best results are usually obtained when at least 5 moles are present.

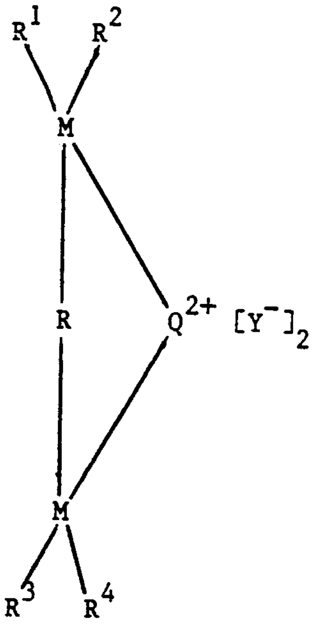
The alkenically unsaturated hydrocarbon will generally be an alkene or a cycloalkene containing 5-30, preferably 5-12, carbon atoms per molecule. Examples of suitable alkenes include the isomeric pentenes, hexenes, octenes and dodecenes, cyclooctene and cyclododecene. Examples of other alkenically unsaturated compounds are styrene, α-methylstyrene, acrylic acid, methacrylic acid, alkyl esters of these acids and dialkenes in which the two unsaturated groups are not conjugated.

Of the palladium and platinum compounds the palladium compounds are the most preferred and it is with reference to palladium compounds that hereinafter the process according to the invention is described in more detail. However, this should not be taken as a restriction; the use of platinum compounds remains possible.

Both homogeneous and heterogeneous palladium compounds can be used. Homogeneous systems are preferred. Suitable palladium compounds are salts of palladium with, for example, nitric acid, sulphuric acid or alkanoic acids containing not more than 12 carbon atoms per molecule. Salts of hydrohalogenic acids can in principle be used as well, but they have the drawback that the halogen ion may produce corrosion. Palladium carboxylates are the preferred catalyst compounds, in particular palladium acetate. Further, palladium acetylacetonate can also be used. Palladium on carbon and palladium combined with an ion exchanger are examples of suitable heterogeneous palladium compounds.

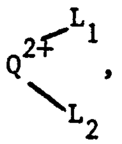
The quantity of palladium, palladium compound, platinum and/or platinum compound is not critical. Preference is given to the use of quantities in the range of from 10^{-8} to 10^{-1} mol of palladium, palladium compound, platinum and/or platinum compound per mol of alkenically unsaturated compound to be hydroformylated. The molar ratio of alkenically unsaturated hydrocarbon to CO will generally range from 5:95 to 95:5, preferably from 1:5 to 5:1.

In the bidentate ligand substituents offering steric hindrance should be absent, which means that no substituents may be present that are able to hinder the formation of complex compounds having the general formula I



I

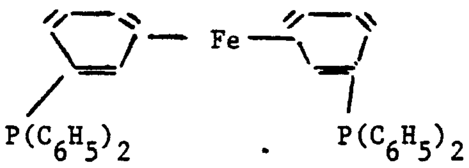
In that formula, Q represents Pt or Pd, Y represents a non-coordinating anion, whilst Q^{2+} can also be written as



in which the ligands L_1 and L_2 are weakly coordinated solvent ligands, e.g. acetonitrile, methanol, acetone, or acetylacetone, or correspond with those employed in the palladium compounds described in the preceding paragraph.

In the bidentate ligand, M is preferably phosphorus. Hydrocarbon groups R^1, R^2, R^3 and R^4 will as a rule contain 2 to 18 carbons atoms, preferably 6 to 14 carbon atoms. Aryl groups are the most suitable, in particular the phenyl groups. Preferred bridging groups -R-are those having the formula (CR^5R^6) in which R^5 and R^6 are hydrogen atoms or hydrocarbon groups offering no steric hindrance and n is 3 or 4. Substituents R^5 and R^6 are preferably hydrogen atoms. The bridging groups R may also make part of cyclic structure, e.g. an aromatic or cycloaliphatic group, the carbon to carbon bond or bonds in the bridge may be saturated or unsaturated and in the bridge or in the cyclic or non-cyclic groups attached to the bridge one or more hetero atoms, e.g. sulphur, oxygen, iron or nitrogen, may have been substituted for carbon atoms, other than the two carbon atoms which must be present in the bridge linking both atoms M.

Examples of suitable bidentate ligands are
1,3-di(diphenylphosphino)propane,
1,4-di(diphenylphosphino)butane,
2,3-dimethyl-1,4-di(diphenylphosphino)butane,
1,4-di(dicyclohexylphosphino)butane,
1,3-di(di-p-tolylphosphino)propane,
1,4-di(di-p-methoxyphenylphosphino)butane,
2,3-di(diphenylphosphino)-2-butene,
1,3-di(diphenylphosphino)-2-oxopropane,
2-methyl-2-(methyldiphenylphosphino)-1,3-di(diphenylphosphino)propane,
0,0'-di(diphenylphosphino)biphenyl,
1,2-di(diphenylphosphino)benzene,
2,3-di(dipenylphosphino)naphthalene,
1,2-di(diphenylphosphino)cylcohexane,
2,2-dimethyl-4,5-di(diphenylphosphino)dioxolane and



It is observed that compounds having a structure like 2-methyl-2-(methyldiphenylphosphino)-1,3-di(diphenylphosphino)-propane, CH_3-C-(CH_2-P(C_6H_5)$_2$)$_3$, although being trifunctional, are nevertheless considered bidentate ligands in the terms of this invention since only two of the three phosphorous atoms can coordinate with the palladium or platinum atom in complex (I).

The bidentate ligand can be employed in quantities which may vary within wide limits, e.g. of from 0.1 to 10 mol per mol of palladium, palladium compound, platinum and/or platinum compound. Preferred quantities lie between 0.33 and 5 mol per mol.

The hydroformylation according to the invention is preferably carried out at a temperature between 20 and 200 °C, in particular between 50 and 150 °C. The overall pressure preferably lies between 1 and 100, in particular 20 and 75, bar above atmopsheric pressure.

The process according to the present invention can be carried out suitably using a molar ratio of carbon monoxide to hydrogen of 1:1 which is the stoichiometric ratio to produce aldehydes. Excess carbon monoxide or hydogen over the stoichiometric amount as indicated hereinbefore may be present, for instance in a molar ratio between 12:1 and 1:12. Good results have been obtained using a carbon monoxide:hydrogen ratio of 1:1.

The process according to the present invention can be carried out conveniently in the presence of an aprotic solvent. A variety of solvents can be applied such as ketones, e.g. acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone and cyclohexanone; ethers, such as the dimethylether of diethylene glycol (also referred to as "diglyme"), anisole, diphenyl ether; aromatic compounds, such as benzene, toluene and the three xylenes; halogenated aromatic compounds, such as chlorobenzene and ortho-dichlorobenzene; halogenated paraffinic hydrocarbons, such as methylene chloride and carbontetrachloride; paraffins such as hexane, heptane, cyclohexane, methylcyclohexane and iso-octane; nitriles, such as benzonitrile and acetonitrile and esters such as methyl benzoate. Good results have been obtained using methyl benzoate. Also mixtures of solvents can be suitably applied. It is also possible to use an excess of the starting material as well as of one or more of the appropriate ligands as solvent(s).

When desired the reaction mixture obtained may be subjected to a catalytic hydrogenation, e.g. over a Raney-Ni catalyst to convert part or all of the aldehyde produced into the corresponding alcohol. The reaction conditions to be applied are well known in the art.

The process according to the present invention can be readily carried out using well-known chemical engineering practice which includes continuous, semi-continuous and batch operation. The reaction time may vary between wide limits, from a couple of minutes to several hours depending on the specific olefin and catalytic system applied. After the reaction the reaction mixture is worked up by techniques known in the art. The product aldehyde can be removed by various means, e.g. by distillation. It is also possible to recycle part or all of the reaction mixture together with the catalytic system.

The following Examples further illustrate the invention.

Examples 1-11 and Comparative Experiments A-G

All experiments were carried out in a 300 ml -Hastelloy C autoclave ("Hastelloy" is a trade name). The autoclave was charged with octene, a solvent (30 ml), a palladium, platinum or ruthenium compound, a ligand and an acid. The Table hereinafter shows which components and how much thereof was used in each experiment. In the Table "*p*" denotes a phenyl group, "Acac" denotes "acetylacetonate" and "pTsA" denotes p-toluenesulphonic acid. The i-octenes consisted of 2.5 %mol 1-octene, 39 %mol 2-octene, 39 %mol 3-octene and 19.5 %mol 4-octene.

The autoclave was then pressurized with an equimolar mixture of carbon monoxide and hydrogen until an initial pressure of 68 bar was reached. The temperature was raised to a value indicated in the Table and the reaction mixture was kept at this temper ature for the time stated in the Table. The reaction mixture was then allowed to cool and was analysed thereafter using gas-liquid chromatography. The results are presented in the Table. The "selectivity to nonanals", expressed in a percentage, is defined as 100 $\times$ a/b, in which "a" is the amount of nonanals in the product and "b" is the sum of the amounts of nonanals, nonanols and nonanes in the product. The "linearity of nonanals" is defined as the percentage of n-nonanal among the nonanals. The "selectivity to alkanes", expressed in a percentage, is defined as 100 $\times$ c/b, in which "c" is the amount of alkanes in the product and "b" is as defined hereinbefore.

Comparison of Examples 1, 2 and 3 shows that the presence of at least 5 equivalents of the acid per gram atom of palladium enhances 1-octene conversion.

Examples 6 to 11 show that the mixture of 1-, 2-, 3-and 4-octenes is easily hydroformylated in a variety of aprotic solvents, producing nonanals of high linearity; the highest conversion has been obtained in Example 9 with methyl benzoate.

Comparative Experiments A and B show that the presence of monodentate ligands has no catalytic action.

Comparative Experiments C and E show that the presence of acetic acid or p-toluenesulphonic acid, respectively, has no catalytic action and Comparative Experiment D shows that the presence of benzenephosphonic acid has only little catalytic action.

Comparative Experiment F shows that the presence of ruthenium acetylacetonate has little catalytic action.

Comparative Experiment G shows that 1,2-di(diphenylphosphino)ethane has only little catalytic action.

TABLE

Example	Comp. Exp.	Catalytic System (mmol)			Octene ml	Temp. °C	Solvent ml	Time h	Octene Conversion, %	Selectivity to Nonanals, %	Linearity of Nonanals, %	Selectivity to alkanes, %
1		Pd acetate(0.1)	$\rho_2P(CH_2)_3P\rho_2$(0.3)	CF_3COOH(2)	1-octene(10)	100	diglyme	5	41	100	71.9	0
	A	ditto	$P\rho_3$(3)	ditto(4)	ditto	135	ditto	ditto	0	-	-	-
	B	ditto	ditto(0.5)	ditto(1)	ditto	125	ditto	ditto	0	-	-	-
2		ditto	$\rho_2P(CH_2)_3P\rho_2$(0.3)	ditto(1)	1-octene(20)	125	ditto	ditto	39.7	100	72.6	0
3		ditto	ditto	ditto(0.5)	ditto	ditto	ditto	ditto	17.1	100	83.2	0
4		ditto	ditto	ditto(2)	ditto	ditto	toluene	ditto	30.2	93.0	69.9	< 2
	C	ditto	ditto	CH_3COOH(4)	ditto	ditto	diglyme	ditto	0	-	-	-
	D	ditto	ditto	$H_2PO_3\rho$(1)	ditto	ditto	toluene	ditto	14	100	62.4	0
	E	ditto	ditto	PTsA(2)	ditto	ditto	ditto	ditto	0	-	-	-
5		$Pt(Acac)_2$(0.1)	ditto	CF_3COOH(2)	ditto	ditto	ditto	ditto	23	96	64.3	1.6
	F	$Ru(Acac)_3$(0.1)	$\rho_2P(CH_2)_4P\rho_2$(0.3.)	ditto(1)	ditto	ditto	ditto	ditto	4	95	64.6	< 1
6		Pd acetate(0.4)	ditto(1.2)	ditto(4)	1-octenes(20)	155	ditto	ditto	30	88.2	69.0	5.9
7		ditto	ditto	ditto	ditto	125	anisole	10	64	91.4	66.7	1.3
8		ditto	ditto	ditto	ditto	ditto	diphenyl ether	ditto	58	97	66.5	1.5
9		ditto	ditto	ditto	ditto	145	methyl benzoate	ditto	67	85	65.9	2.6

TABLE (cont'd)

Example	Comparative Experiment	Catalytic System (mmol)			1-Octene ml	Temp. °C	Solvent ml	Time h	Octene Conversion, %	Selectivity to Nonanals, %	Linearity of Nonanals, %	Selectivity to alkanes, %
10		ditto	ditto	ditto(8)	ditto	125	anisole	ditto	64	73	67.9	2.8
11		ditto	ditto	ditto(4)	ditto	ditto	o-dichloro-benzene	ditto	59	87	72.3	4.0
	G	ditto(0.1)	$\rho_2P(CH_2)_2P\rho_2$(0.3)	ditto(2)	1-octene(10)	110	diglyme	5	5	100	64.1	0

Claims

1. Process for the preparation of aldehydes by hydroformylation of an alkenically unsaturated compound having at least 5 carbon atoms per molecule, in which an alkenically unsaturated compound is contacted with carbon monoxide and hydrogen in the +presence of an aprotic solvent and a catalytic system based on

a) palladium, a palladium compound, platinum and/or a platinum compound,

b) an anion of a carboxylic acid with a $pK_a < 2$, measured in aqueous solution at 18 °C, and

c) a bidentate ligand of the general formula R^1R^2-M-R-M-R^3R^4, wherein M represents phosphorus, arsenic or antimony, R represents a divalent organic bridging group having at least three carbon atoms in the bridge, none of these carbon atoms carrying substituents that may cause steric hindrance, and R^1, R^2, R^3 and R^4 are similar or dissimilar optionally substituted hydrocarbon groups.

2. A process as claimed in claim 1, in which the carboxylic acid is trifluoroacetic acid.

3. A process as claimed in claim 1 or 2, in which 1 to 50 mol of said anion of a carboxylic acid is used per gram atom palladium and/or platinum.

4. A process as claimed in any one of the preceding claims, in which the hydrocarbon groups R^1, R^2, R^3 and R^4 are aryl groups containing 6-14 carbon atoms.

5. A process as claimed in claim 4, in which the aryl groups are phenyl groups.

6. A process as claimed in any one of the preceding claims, in which 0.1-10 mol of bidentate ligand is used per mol of palladium, palladium compound, platinum and/or platinum compound.

7. A process as claimed in any one of the preceding claims, in which a palladium compound is used.

8. A process as claimed in any one of the preceding claims, in which a phosphine is employed as bidentate ligand.

9. A process as claimed in any one of the preceding claims, in which R represents a trimethylene group.

10. A process as claimed in any one of the preceding claims, in which the ligand is 1,3-di-(diphenylphosphino)propane or 1,4-di-(diphenylphosphino)butane.

11. A process as claimed in any one of the preceding claims, in which the alkenically unsaturated hydrocarbon is an alkene.

European Patent
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EUROPEAN SEARCH REPORT

Application number
EP 86201781.1

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US - A - 4 467 116 (PETRUS W.N.M. VAN LEEUWEN et al.) * Claim 1 * --	1	C 07 C 45/50 C 07 C 47/02 B 01 J 31/28
A	US - A - 4 317 936 (LED KIM et al.) * Claim 1 * --	1	
A	US - A - 4 390 729 (ALEXIS A. OSWALD) * Claim 1 * --	1	
A	US - A - 4 224 255 (WILLIAM E. SMITH) * Claims 1,7-10,13-15 * --	1	
A	US - A - 4 370 258 (IKUEI OGATA et al.) * Claims 1,4,5 * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 07 C 45/00
C 07 C 47/00
B 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	09-01-1987	REIF

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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